Journal of Magnetic Resonance 193 (2008) 233–242

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

# $^{29}$Si NMR in solid state with CPMG acquisition under MAS

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ARTICLE INFO

*Article history:*
Received 22 February 2008
Revised 8 May 2008
Available online 20 May 2008

*Keywords:*
Solid-state NMR
$^{29}$Si NMR
CPMG acquisition
*J*-coupling
MAS
HETCOR

ABSTRACT

A remarkable enhancement of sensitivity can be often achieved in $^{29}$Si solid-state NMR by applying the well-known Carr–Purcell–Meiboom–Gill (CPMG) train of rotor-synchronized $\pi$ pulses during the detection of silicon magnetization. Here, several one- and two-dimensional (1D and 2D) techniques are used to demonstrate the capabilities of this approach. Examples include 1D $^{29}$Si{X} CPMAS spectra and 2D $^{29}$Si{X} HETCOR spectra of mesoporous silicas, zeolites and minerals, where X = $^{1}$H or $^{27}$Al. Data processing methods, experimental strategies and sensitivity limits are discussed and illustrated by experiments. The mechanisms of transverse dephasing of $^{29}$Si nuclei in solids are analyzed. Fast magic angle spinning, at rates between 25 and 40 kHz, is instrumental in achieving the highest sensitivity gain in some of these experiments. In the case of $^{29}$Si–$^{29}$Si double-quantum techniques, CPMG detection can be exploited to measure homonuclear *J*-couplings.



## 1. Introduction

Silicon-29 is one of the most widely studied nuclei in solid-state NMR spectroscopy. Numerous reviews have detailed the applications of $^{29}$Si NMR to the study of silicates [1], silica surfaces [2], silicon alloys [3], ceramics [4], glasses [5], and other crystalline and amorphous materials [6,7]. The vast majority of these studies have relied on one-dimensional (1D) experiments performed using direct $^{29}$Si polarization (DP) or $^{29}$Si{$^{1}$H} cross polarization (CP), magic angle spinning (MAS) and $^{1}$H decoupling using a radiofrequency (RF) magnetic field. Two-dimensional (2D) methods have also been employed, e.g., in CP-based $^{29}$Si{$^{1}$H} heteronuclear (HETCOR) NMR studies of organic/inorganic nanocomposites [8–11], zeolites [12], silica [13], and mesoporous aluminosilicates [14]. Two-dimensional methods for obtaining $^{29}$Si–$^{29}$Si correlation spectra that exploit double-quantum (DQ) through-bond (scalar) or through-space (dipolar) interactions have been reported, as well [15–17].

However, wider exploitation of multi-dimensional solid-state NMR methods is hindered by low $^{29}$Si sensitivity, which results from low natural abundance of spin-1/2 isotope (4.7%), small gyromagnetic ratio, and unusually slow longitudinal relaxation. Fortunately, the presence of a long relaxation time $T_1$ in inorganic solids is often accompanied by a long transverse dephasing (decoherence) time $T_2^{CPMG}$, defined here as the decay time of the echo train due to time-dependent interactions that are non-refocusable by the Carr–Purcell–Meiboom–Gill [18] (CPMG) sequence of $\pi$ pulses combined with MAS and/or RF decoupling schemes. This makes it possible to detect the signal multiple times at intervals that are longer than the free induction decay (FID) observed following the single-pulse excitation (often denoted as $T_2^*$) but much shorter than $T_1$.

The multiple pulse CPMG sequence, which refocuses inhomogeneous line broadening and reduces homonuclear dipolar broadening in solids, was first introduced to measure the decay of transverse nuclear magnetization [19,20]. It later found applications in various areas of magnetic resonance spectroscopy, including experiments with field gradients or strongly inhomogeneous static fields (e.g., imaging [21–23] and diffusion measurements [24–26]), high-resolution liquid-state NMR (solvent peak suppression [27,28], HETCOR experiments [29–31], and exchange studies [32]), homonuclear distance measurements in solids [33,34] and electron spin resonance (ESR) [35,36].

In solid-state NMR applications, the most appealing advantage offered by the CPMG pulse sequence is the sensitivity gain resulting from refocusing the magnetization multiple times. Indeed, enhancement of the signal-to-noise (S/N) ratio has been demonstrated in various studies where low natural abundance, a low gyromagnetic ratio ($\gamma$), long relaxation time $T_1$, large line width or any combination of these factors rendered 'standard' averaging of FIDs impractical. These studies used static [37–42], MAS [40,41,43], MQMAS [44,45], and PHORMAT [46] experiments with spin-1/2 and quadrupolar nuclei.

In spite of long decoherence times of silicon nuclei, the CPMG technique has been used only rarely in $^{29}$Si NMR. The strategy was applied in a study of silicates (α-crystobalite and Zircon), where the sensitivity of $^{29}$Si MAS spectra was increased by an order of magnitude using a rotor-synchronized CPMG sequence [47] and

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doi:10.1016/j.jmr.2008.05.007

at least fivefold signal enhancement was reported in 2D $^{29}$Si{$^{1}$H} heteronuclear correlation (HETCOR) experiments on clay minerals, where the $^{29}$Si signal was stretched by means of multiple echoes at the expense of the chemical shift information [48].

We recently demonstrated that highly resolved $^{29}$Si{$^{1}$H} HETCOR NMR spectra of silica-based catalytic systems can be obtained with excellent sensitivity using multiple pulse CPMG refocusing and appropriate data processing [49,50]. These experiments were made possible by the use of fast MAS, at rates of 25–40 kHz, which provided adequate $^{1}$H–$^{1}$H decoupling. More importantly, fast MAS allowed the heteronuclear decoupling to be performed using low RF power, which was essential in these experiments due to unusually long acquisition periods (up to several seconds).

Herein, we analyze the utility of CPMG refocusing in a number $^{29}$Si NMR techniques, and discuss the experimental strategies that maximize sensitivity, as well as the future applications of these methods. Examples of 1D $^{29}$Si{X} CPMAS spectra, 2D $^{29}$Si{X} HETCOR (X = $^{1}$H and $^{27}$Al) spectra and $^{29}$Si–$^{29}$Si DQMAS homonuclear correlation spectra are shown. This effort was largely motivated by our interest in studying the mesoporous catalytic materials, which is reflected in the choice of samples for this study.

## 2. Experimental

### 2.1. NMR resonance

Most of the experiments were performed at 14.1 T on a Varian NMR System 600 spectrometer, equipped with 3.2 and 1.6 mm triple-resonance MAS probes, which can accommodate 22 and 8 μL of sample and reach rotation frequencies of 25 and 45 kHz, respectively. The $^{29}$Si{$^{27}$Al} and DQ $^{29}$Si–$^{29}$Si{$^{1}$H} spectra were acquired at 9.4 T on a Chemagnetics Infinity spectrometer using 5 mm triple-resonance probe operated at the MAS rates of 8–10 kHz. The pulse sequence used in 2D $^{29}$Si{X} experiments (Fig. 1a) is similar to that used in our earlier study [49]. The same sequence was used in 1D CPMAS experiments by setting $t_1 = 0$. The DQMAS homonuclear correlation experiments (Fig. 1b) utilized the $^{29}$Si{$^{1}$H} CP followed by the INADEQUATE scheme for excitation and reconversion of DQ coherences [51–53]. The $\pi$ pulses were always applied synchronously with the rotor.

The experimental parameters are given in figure captions using the following symbols: $B_0$ denotes the magnetic field strength, $\nu_R$ the sample rotation rate, $\nu_{RF}^X$ the magnitude of the RF magnetic field applied to the X spins, $\tau_{CP}$ the cross polarization time, $N_{CPMG}$ the number of echoes acquired in CPMG experiments, $\tau_{CPMG}$ the corresponding time interval between $\pi$ pulses, $\tau_{RD}$ the relaxation delay, and NS the number of scans. The chemical shifts of $^{1}$H, $^{29}$Si, and $^{27}$Al are reported using the $\delta$ scale and are referenced to tetramethylsilane (TMS) and 1 M aluminum(III) nitrate ($Al(NO_3)_3$) solution at 0 ppm.

### 2.2. Samples

Most of the CPMG-based experiments are conducted using three samples of MCM-41-type mesoporous silica nanoparticle (MSN) materials whose synthesis and characterization have been described in our earlier reports: (i) a non-functionalized sample, referred to as MSN [54]; (ii) a sample functionalized via co-condensation with covalently bound allyl groups (—$CH_2$—CH=$CH_2$), referred to as AL–MSN [54]; and (iii) a sample functionalized via grafting with chloromethyltriethoxysilane (($EtO)_3Si(CH_2Cl)$), referred to as CMTES–MSN [50]. Based on the deconvolution of $^{29}$Si DPMAS spectra, we estimated that 11 ± 2% and 15 ± 2% of all silicon atoms in AL–MSN and CMTES–MSN, respectively, are bound to carbon (functionalized) [50,54]. All silicas were studied in the absence of templating molecules, which were removed by acid extraction (MSN and AL–MSN) or calcination (CMTES–MSN). The measurements were typically performed with samples packed in MAS rotors after exposure to ambient conditions in the laboratory. In the case of AL–MSN the spectra were obtained after the inorganic hydrogen atoms on the surface had been eliminated by exchange with deuterium. For these measurements the material was packed using a glove bag.

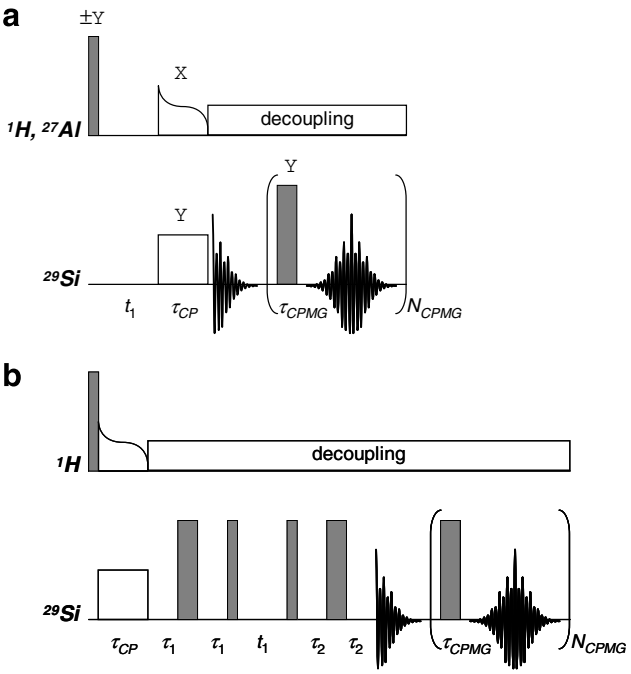


**Fig. 1.** Pulse sequences for 2D $^{29}$Si NMR experiments with CPMG detection: (a) $^{29}$Si{$^{1}$H} and $^{29}$Si{$^{27}$Al} HETCOR, (b) $^{29}$Si–$^{29}$Si{$^{1}$H} refocused INADEQUATE. Solid rectangles represent $\pi$ and $\pi/2$ pulses, whereas open pulses represent cross polarization and decoupling. In sequence (a), the phases are the same as in reference [49], with the receiver phase being inverted in concert with the phase of $\pi/2$ pulse in the $^{1}$H channel. In sequence (b), the phase cycling during INADEQUATE is the same as in reference [53]. The phases of $\pi$ pulses used in the CPMG sequence followed the phase of the last (refocusing) pulse in INADEQUATE. In addition, the hypercomplex method was used to achieve quadrature detection in the $v_1$ dimension in all 2D experiments.

To demonstrate the $^{29}$Si{$^{27}$Al} methods, two commercially available samples were used. Andesine (sodium calcium aluminum silicate, $Na_{0.7-0.5}Ca_{0.3-0.5}Al_{1.3-1.5}Si_{2.7-2.5}O_8$) is a naturally occurring mineral belonging to the plagioclase series of the feldspar family. Plagioclase is a solid solution series, also known as the plagioclase feldspar series, which ranges from albite ($NaAlSi_3O_8$) to anorthite ($CaAl_2Si_2O_8$). The sample was purchased from Alfa Aesar, ground in a mortar to a fine powder and used without further treatment. Zeolite 13X was purchased from Research Chemicals Ltd., and also used without further treatment.

## 3. Data processing and sensitivity gain

Figs. 2a and 3a show examples of echo trains induced in andesine and in AL–MSN by the CPMG sequence $(CP)_Y$–$[\tau_{CPMG}$–$(\pi)_Y$–$\tau_{CPMG}$–echo$]_{N_{CPMG}}$ (as shown in Fig. 1a, with $t_1 = 0$). Blanking of the receiver was applied during the $\pi$ pulses to eliminate the spurious signals associated with high-power RF irradiation. In andesine, the polarization was transferred from the $^{27}$Al nuclei, whereas in AL–MSN the initial excitation was applied to protons in the allyl groups. Both samples yielded very long echo trains (see the discussion of transverse dephasing in Section 4), which